

STUDY OF IMPROVED BERYLLIUM
OXIDE MATERIALS FOR MICROELECTRONICS
TECHNOLOGY

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Period 1 September - 31 October 1963
Contract NASw-685

Submitted by
National Beryllia Corporation
Hackensack, New Jersey

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(1) BACKGROUND

The objectives of the present program have been the development of techniques for the growth of single crystals of beryllium oxide suitable for use in microelectronic applications, and the precise determination of their mechanical, thermal and dielectric properties.

The single crystal growth portion of the program has had as its main objective the perfection of techniques for reproducibly growing platelet type crystals of controllable high purity and minimum surface contamination and imperfections.

The thermal and dielectric properties of polycrystalline BeO are well known as well as the basic crystal structure of the material. Several investigators have reported on the piezoelectric and ferroelectric properties of BeO. The testing portion of this program has had as its main objective the precise determination of the anisotropic characteristics of single crystal BeO as evidenced by the orientational sensitivity of the dielectric and thermal conducting properties.

(2) TECHNICAL PROGRAM

Task A - Single Crystal Growth

The nucleation and growth of pure, single crystals of BeO has been attempted in two completely different environments. The first of these is by the water-vapor transport method where use is made of a pure BeO system wherein polycrystalline BeO is both the nutrient material and seeding material. The second technique is by crystallization of BeO from alkali molybdate.

1. Water-Vapor Transport Method

Growth by the water-vapor transport method has been the most successful method of preparing single crystals of BeO. The experiments performed during the period are outlined in Table I. Crystals grown by this technique have been hexagonal in cross-section with average diameters of 0.050 - 0.060" and many crystals up to 0.175" diameter. Chemical purity of these crystals is better than 99.9%. Surface impurities constitute nearly all of the contamination. The main sources of contamination are in the incoming carrier gas containing reactive steam, and in the nutrient BeO materials. The reaction chamber is made of all BeO but there is still possibility of contaminating materials being released from the chamber walls as a result of corrosive attack by water vapor. The presence of vapor phase contaminants in the chamber may be strongly affecting the size to which a crystal may grow. Surface contamination of a growing crystal could be sufficient to upset the thermodynamic conditions conducive to continue growth. The presence of this contamination on the surface can then prevent continued growth by not affording an effective nucleation activity. Some evidence has been seen supporting this type of reason.

During this period several experiments have been run where the seed plates were pre-treated with hydrofluoric and hydrofluorosilicic acids. Crystal nucleation was greater in the regions treated with hydrofluoric acid, and less in regions treated with hydrofluorosilicic acid. This difference is believed to be due to the leaching out of impurities from the surface of the seed plate, and can be considered similar to the different nucleation/growth potentials at the surface of growing and contaminated crystals. This similarity and knowledge of the role of impurities in the flux growth method and in the evaporation-condensation process point up quite strongly the need for observing the controls set forth in previous reports and especially those pertaining to the purity of the system.

TABLE I

WATER-VAPOR TRANSPORT EXPERIMENTS CRYSTAL GROWTH

<u>Run No.</u>	<u>Carrier Gas</u>	<u>Gas Flow Rate</u>	<u>Vaporizer Temp.</u>	<u>Water Flow Rate</u>	<u>Operating Temp.</u>	<u>Time At Temp.</u>	<u>Results</u>
18	He	1 L/min.	175°C	2 cc/min.	--	--	Slight Tube blocked Bad run.
19	He	1 L/min.	160°C	2 cc/min.	1800°C	2hr. 30min.	Slight growth on sharp edges. Fibrous growth in regions pre-treated with hydrofluosilicic acid.
20	He	2 L/min.	185°C	2 cc/min.	1775°C	1 hr. 30min.	Very good yield- Many platelets up to 3/16" across- Some discoloration. Best yield in region pre-treated with HF.
21	He	1 L/min.	195°C	2 cc/min.	1795°C	2hrs.	Poor yield -Difficul- ty with hot plate for vaporizer.
22	He	1 L/min.	190°C	2 cc/min.	1950°C	2hrs.	BeO reaction tube shifted. Some growth in regions pre- treated with HCl and HF.
23	He	1 L/min.	180°C	2 cc/min.	1795°C	2hrs.	Fibrous growth - No platelets.

2. Solution Growth Experiments

Preliminary experimental runs were made with the platinum-wound furnace. At temperatures in the vicinity of 1375°C a reaction occurred between the platinum winding and the Al_2O_3 muffle. After several attempts to make use of the platinum-wound furnace, it became evident that the present system was not compatible with the MoO_3 vapors above the solution. A second solution growth furnace was constructed using Glocar heating elements and an Al_2O_3 muffle. The furnace was calibrated in the temperature range $1300 - 1500^{\circ}\text{C}$, and several solubility experiments were run to determine the best operating conditions and growth parameters. Table II lists these experimental runs and their results. Use has been made of both Li_2MoO_4 and $\text{Li}_2\text{Mo}_2\text{O}_7$ with MoO_3 and spherical BeO powder (-325 mesh). Results to date indicate that Li_2MoO_4 with excess MoO_3 is better than $\text{Li}_2\text{Mo}_2\text{O}_7$ with excess MoO_3 . It is also indicated that the Li_2MoO_4 made from LiOH and MoO_3 was better than the commercially available Li_2MoO_4 ; the reason probably being associated with the 17.2% excess Li_2O present in the commercially available material.

Data indicate that at 1455°C approximately 0.25 mole of BeO may be dissolved in $\text{Li}_2\text{MoO}_4:1.25 \text{ MoO}_3$. Crystallization of BeO microcrystals was accomplished at 1425°C after a mixture of Li_2MoO_4 , MoO_3 and BeO (Molar ratio 1:1.25:0.5, respectively) was heated to 1455°C for a period of 36 hours then held at 1425°C for 48 hours. These crystals were no more than $0.005 - 0.010''$ in cross section but displayed many of the physical characteristics associated with crystals grown from alkali molybdate solutions by other investigators.

The identifying characteristics include complete transparency, hexagonal cross-section, and hemi-pyramidal growths from the basal surface. Growth rates have been reported in the vicinity of $0.001''$ per day. Growth rates with Li_2MoO_4 made up by National Beryllia appear to be somewhat faster and continued efforts will be directed toward perfection of the process to produce larger crystals faster.

For better control and faster growth, an artificial temperature gradient has been built into the system using BeO heat sink blocks and BeO rod ($1/4'' \times 1'' \times 3 1/4''$) between the heat sink and the platinum reaction crucible. With this set of conditions it is possible to maintain a temperature of 1455°C on the platinum crucible and 1325°C on the heat sink end of the heat transfer rod. One additional heat transfer rod will be introduced between the melt and the heat sink to complete the necessary artificial gradient. This design offers the possibility of securing a definite and controllable thermal extraction area.

TABLE II
SOLUTION GROWTH EXPERIMENTS

Run No.	Furnace Charge	Solution Crystallization				Results
		Temp.	Time	Temp.	Time	
1	$\text{Li}_2\text{MoO}_4(\text{NBC}) : \text{BeO}$ 1 : 2	1425°C	24 hrs.	1400°C	36hrs.	Undissolved
2	$\text{Li}_2\text{MoO}_4(\text{NBC}) : \text{BeO}$ 1 : 2	1495°C	24hrs.	1400°C	48hrs.	Partially dissolved. No crystallization.
3	$\text{Li}_2\text{MoO}_4(\text{NBC}) : \text{BeO} : \text{MoO}_3$ 1 : 2 : 2	1460°C	36hrs.	1440°C	36hrs.	BeO partially dissolved. Some rejection of very small BeO crystals.
4	$\text{Li}_2\text{Mo}_2\text{O}_7 : \text{MoO}_3 : \text{BeO}$ 1 : 1.25 : 1	1460°C	24hrs.	1440°C	24 hrs.	Discolored-Some dissolution. No crystallization.
5	$\text{Li}_2\text{Mo}_2\text{O}_7 : \text{BeO}$ 1 : 0.5	1460°C	36hrs.	1440°C	72hrs.	Partially dissolved No crystallization.
6	$\text{Li}_2\text{MoO}_4(\text{NBC}) : \text{MoO}_3 : \text{BeO}$ 1 : 1.25 : 0.5	1460°C	36hrs.	1445°C	48hrs.	Mostly dissolved. Slight crystallization.
7	$\text{Li}_2\text{MoO}_4(\text{NBC}) : \text{MoO}_3 : \text{BeO}$ 1 : 1.25 : 0.5	1455°C	36hrs.	1425°C	48hrs.	Mostly dissolved. Crystallization of small BeO platelets up to 0.005 - 0.010" long.

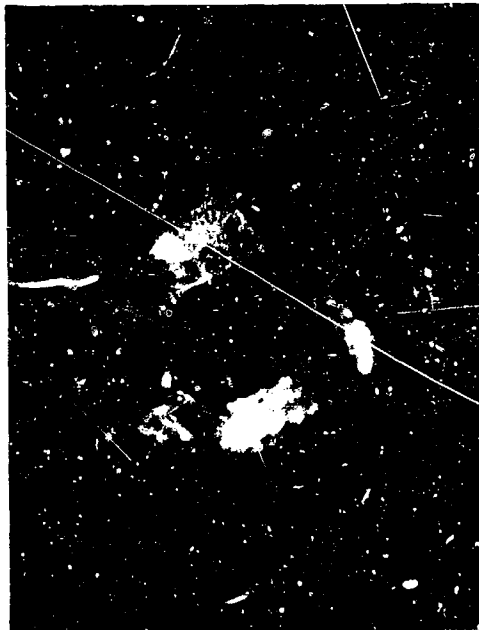


FIGURE 1
PHOTOMICROGRAPHS OF MICROCRYSTALS
FROM SOLUTION GROWTH EXPERIMENTS

Task B - Dielectric, Optical and Thermal Properties

1. Dielectric Properties

During this reporting period considerable use has been made of the General Radio Model 1015A capacitance bridge assembly with the BeO crystal dielectric sample holder No. 1 and No. 2 described in previous reports.

Figures 2 and 3 show a plot of capacitance as a function of distance between electrodes for sample holders 1 and 2. These data were used in calibration of the sample holders with and without concentric metal shields. It was found that metal shields were not necessary and, in fact, led to misinterpretation of data. The small diameter of the shield introduced error into the system through the added high lead-to-shield capacitance. Data gained on both sample holders without a shield was more reliable, realistic and reproducible. In the case of the sample holder No. 2, the design of the holder itself affords sufficient shielding except in a case where a fluorescent loop light is operated very close to the test apparatus. In this case the 60 cycle pickup by the bridge assembly appears to have a greater effect on the readings than sample interference. Capacitance readings shown in Tables III and IV are representative of the capacitance of the complete holder, which should remain constant and the varying capacitance of the air gap. The composite capacitance is shown as a function of the electrode spacing. The difference in sample holder unit capacitance accounts for the difference in capacitance readings for the two holders with the same electrode spacing. One additional alteration was necessary to improve the quality of the readings. This involved the reworking of the ground electrode to produce two equal diameter electrode points, and prevented the inclusion of stray capacitance readings around the edges of the BeO crystals (Figure 4).

Preliminary calibration of the unit using sample specimens of polycrystalline BeO between 0.092" and 0.012" thick was completed prior to initiating tests on single crystals. Data gained from this calibration - standardization portion of the program pointed up several important facts useful in later testing of single crystals.

Dielectric measurements on single crystal platelets of BeO were first made using two electrodes of different cross-sectional areas. The high lead was 0.050" diameter with a low angle taper; the ground electrode was a pedestal of uniform 0.190" diameter. The single crystal samples were positioned between the unit electrodes with silver paste squeezed into surface-conforming electrodes in contact with both faces of the crystal. Capacitance readings were taken and the electrode areas were measured. Several faults were found with this type of set-up.

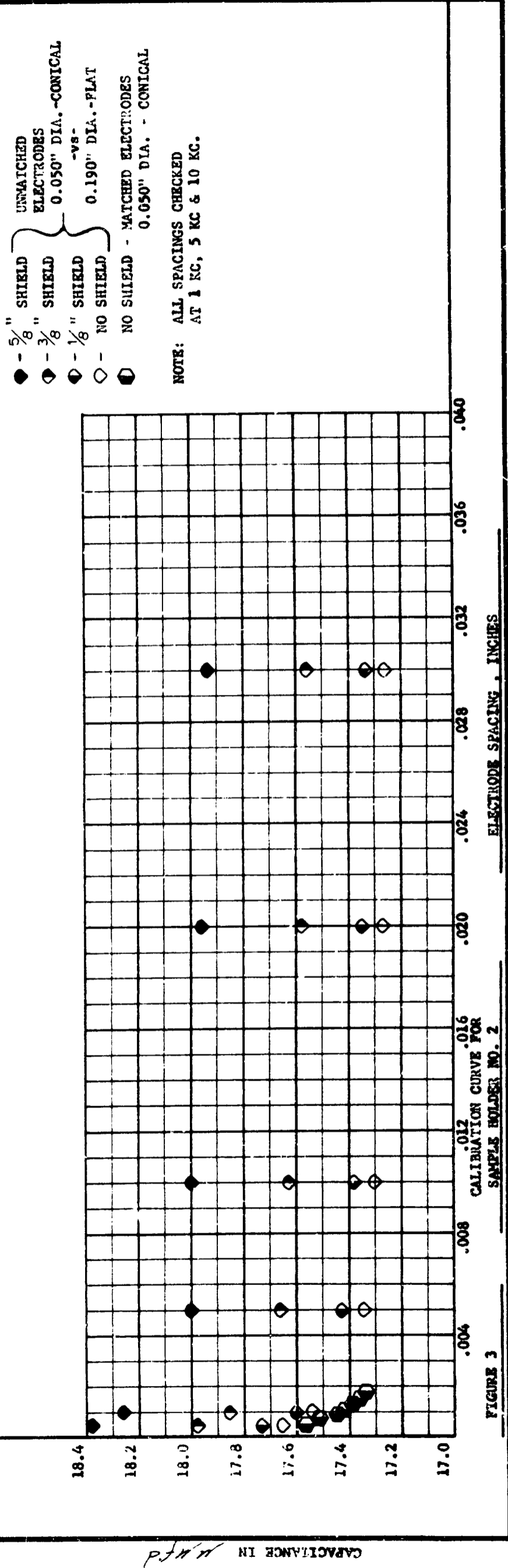
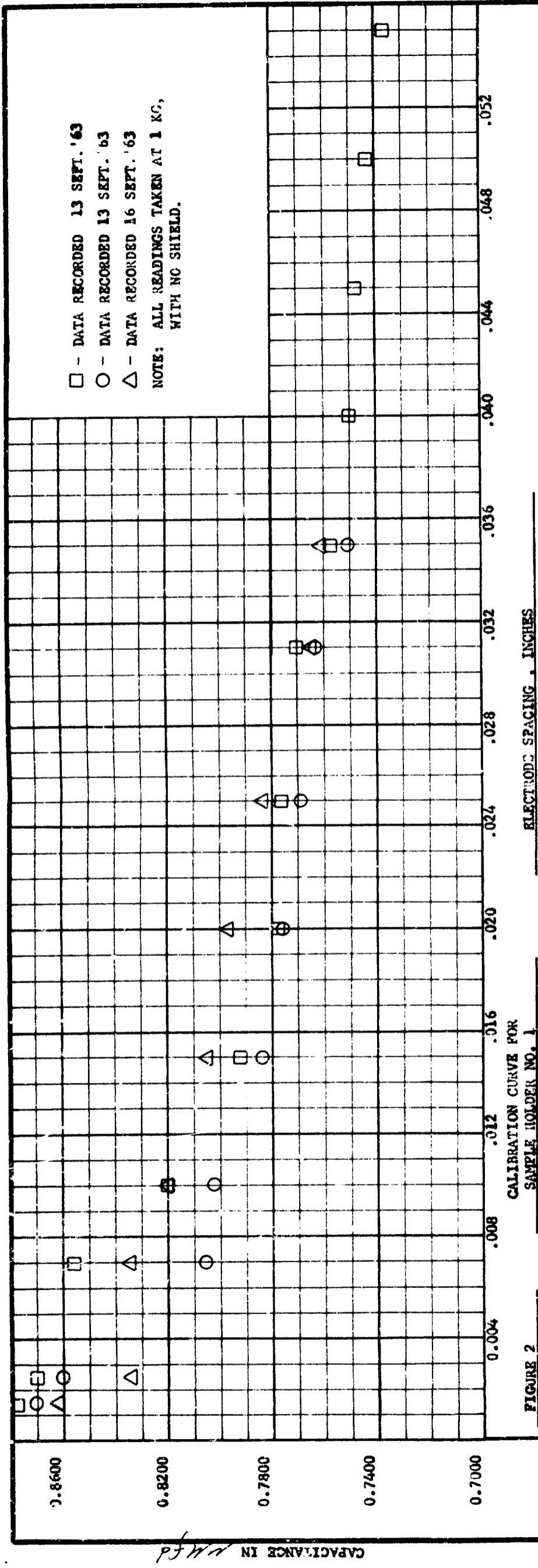


TABLE I.I
CALIBRATION DATA FOR DIELECTRIC
SAMPLE HOLDER NO.1

<u>Electrode Spacing</u>	<u>Frequency</u>	<u>Capacitance</u>	<u>Dissipation Factor</u>
0.0015"	1 KC	0.8700	0.0090
0.0025"	1 KC	0.8600	0.0090
0.007	1 KC	0.8140	0.009
0.010	1 KC	0.8050	0.009
0.015	1 KC	0.7850	0.0087
0.020	1 KC	0.7770	0.0099
0.025	1 KC	0.7700	0.0096
0.031	1 KC	0.7630	0.0095
0.035	1 KC	0.7530	0.0090
0.0415	1 KC	0.8630	0.0094
0.0025	1 KC	0.8340	0.0080
0.007	1 KC	0.8330	0.0090
0.010	1 KC	0.8200	0.0090
0.015	1 KC	0.8060	0.0090
0.020	1 KC	0.7950	0.0080
0.025	1 KC	0.7840	0.0080
0.031	1 KC	0.7640	0.0090
0.035	1 KC	0.7590	0.0097

TABLE IV

CALIBRATION DATA FOR DIELECTRIC
SAMPLE HOLDER NO. 2 WITH EQUAL -
AREA ELECTRODES AND NO SHIELD

<u>Electrode Spacing</u>	<u>Frequency</u>	<u>Capacitance</u>	<u>Dissipation Factor</u>
0.0005"	1 KC	17.5740	0.0020
0.0005"	5 KC	17.5610	0.0055
0.0005"	10 KC	17.5770	0.0100
0.0007"	1 KC	17.5100	0.0020
0.0007"	5 KC	17.4940	0.0055
0.0007"	10 KC	17.5150	0.0100
0.0009"	1 KC	17.4640	0.0020
0.0009"	5 KC	17.4500	0.0055
0.0009"	10 KC	17.4680	0.0100
0.0011"	1 KC	17.4310	0.0020
0.0011"	5 KC	17.4170	0.0055
0.0011"	10 KC	17.4340	0.0100
0.013"	1 KC	17.4040	0.0020
0.013"	5 KC	17.3890	0.0055
0.013"	10 KC	17.4080	0.0100
0.0015"	1 KC	17.3800	0.0020
0.0015"	5 KC	17.3660	0.0055
0.0015"	10 KC	17.3850	0.0100
0.018"	1 KC	17.3570	0.0020
0.018"	5 KC	17.3440	0.0055
0.018"	10 KC	17.3620	0.0100

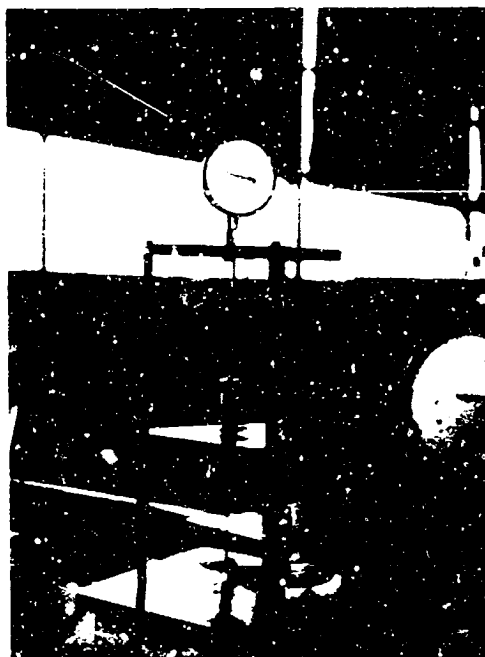


FIGURE 4
PHOTO OF SAMPLE HOLDER NO. 2

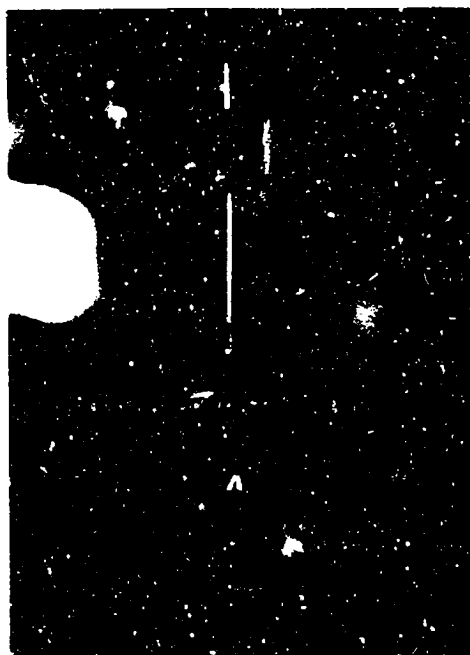


FIGURE 5
PHOTO OF ELECTRODE ASSEMBLY
OF SAMPLE HOLDER NO. 2

- (a) Measurements of exact areas of contact were very poor due to size and irregularity of shape.
- (b) Silver pastes (and other pastes) do not constitute pure metallic electrodes and the contaminants present contribute to the total capacitance of the system.
- (c) As the thickness of the silver paste electrodes varied, the high lead-to-ground stray capacitance varied and was not measureable.
- (d) Handling of crystals and application of pressure were very difficult and in many cases resulted in damage to the crystal.

Following alterations in unit electrode design the following procedure was used in measuring dielectric properties of single crystal BeO platelets.

- (a) Specimen was selected with hexagonal cross-section and surface free of spurious growths and other imperfections.
- (b) Two tin foil electrodes of 0.050" diameter cross-section were fabricated between high lead and ground electrodes of equal cross-section.
- (c) Surfaces of tin foil electrodes were treated with vaseline, and electrodes were positioned on unit electrode tips.
- (d) Single crystal platelet was positioned on foil on ground electrode and high lead electrode was brought in contact using micrometer advance.
- (e) Capacitance measurements were made with several different electrode contact pressures.
- (f) Single crystal specimen was removed to metallograph for exact measurement of thickness.

Table V lists some of the dielectric test data for single crystal BeO platelets. All measurements were made parallel to the c-axis. Polycrystalline BeO has a dielectric constant of 6.3. Sample holder No. 2 was calibrated and standardized with thin layers of polycrystalline BeO produced by cold-pressing and sintering, and by hot-pressing techniques.

The crystal structure of BeO has been well established as a di-hexagonal structure.* Piezoelectric characteristics have been identified and are similar to what one would predict based on the crystal structure and hemi-pyramidal crystal characteristics and the physical response to chemical etching. Predictions on the anisotropic dielectric properties of BeO follow two general trains of thought. One line of thought would predict deviation of the dielectric constant for single crystal material from the average value for polycrystalline material based on the relative inter-atomic distances in the "c" and "a" directions. Cell constants have been determined by x-ray analysis as $a_0 = 2.6979 \pm 0.0002 \text{ \AA}$, and $c_0 = 4.3772 \pm 0.0002 \text{ \AA}$; $c/a = 1.63$. Another line of thought would predict this deviation based upon the relative interplanar distances and the bond distances. In this case the Be-O bond distance parallel to the c-axis is 1.659 \AA , and the Be-O bond distance at $108^\circ 47'$ from the c-axis is 1.645 \AA .

If one considers only the cell constants (c/a ratio of 1.63) he could expect that the dielectric constant in the "c" direction should be less than 6.3, and in the "a" direction should be more than 6.3.

Using the same inter-electron effectiveness reasoning, but considering the interplanar as well as the inter-atomic distances between dissimilar atoms one could expect that the dielectric constant in the "c" direction should be more than 6.3, and in the "a" direction should be less than 6.3. Interplanar distances are 1.659 \AA , and 0.5297 \AA ; interatomic distance between dissimilar atoms on a planar projection is 1.5574 \AA .

Data listed in Table V indicate that the dielectric constant measured in the "c" direction is less than that of polycrystalline BeO. If this data, and the interpretation thereof, is correct, the first line of thought listed above would govern the relationship between dielectric properties in different crystal directions. However, if the data is not correctly interpreted, (that is, if the effect of the vaseline is greater than allowed) the dielectric constant in the "c" direction would be greater than for polycrystalline BeO and the alternate line of reasoning would better describe the anisotropic character of the dielectric properties.

*Smith D. K., Newkirk, H. W., Kahn, J. S., Lawrence Radiation Lab. (Livermore) Rpt. W-7405-eng-48, 4 Oct. 1962.

TABLE V

DIELECTRIC TEST DATA FOR SINGLE CRYSTAL BeO
ALL MEASUREMENTS MADE PARALLEL TO C-AXIS

<u>Identity</u>	<u>Thickness</u>	<u>A/t</u>	<u>Cv</u>	<u>Cx</u>	<u>Frequency</u>	<u>K</u>
CPII 2	0.001"	1.965	0.441	2.4000	1 KC	5.45
				2.3190	10 KC	5.28
				2.6840	1 KC	6.09
				2.6310	5 KC	5.98
				2.6790	10 KC	6.09
CPII 14	0.0018"	1.09	0.2449	1.2220	1 KC	5.0
				1.2770	5 KC	5.25
				1.2970	10 KC	5.32
				1.2910	1 KC	5.29
				1.3290	5 KC	5.44
				1.3440	10 KC	5.51
CPII 15	0.0012"	1.64	0.367	1.6745	1 KC	4.56
				1.6920	5 KC	4.61
				1.6990	10 KC	4.64

2. Optical and Thermal Properties

Work conducted under this portion of the contract during this period was devoted mainly to the investigation of techniques for exact determination of thermal conductivity of single crystal platelets of BeO using the facilities of Queens Laboratory Inc., Edison, New Jersey. A complete report of this work is included as Appendix A to this report

(3) PLANS FOR NEXT REPORTING PERIOD

During the next reporting period work will continue on the solution growth portion of Task A. A concerted effort will be made to produce single crystal BeO by this method of sufficient size for comparative testing with crystals grown by the water-vapor transport method. Determinations will be made of chemical purity of solution grown crystals by x-ray and spectrographic techniques. Optical goniometric techniques will be employed as a means of primary identification and classification of crystals, taking advantage of the transparency and birefringence of BeO. Dielectric property data accumulation will continue and will include measurement of dielectric constant, dissipation factor, and resistivity. It is anticipated that preliminary data relative to the anisotropic characteristics of thermal conductivity of BeO will be available.

(4) Project Personnel

During the reporting period the following National Beryllia Corporation personnel participated in the programs, Dr. E. Ryshkewitch, P. S. Hessinger, R. L. Sharkitt, K. Styhr, and G. Ferment.

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STUDY OF IMPROVED BERYLLIUM OXIDE
MATERIALS FOR MICROELECTRONICS TECHNOLOGY

Appendix A
To
Bi-Monthly Report for the Period
1 September - 31 October, 1963
Contract NASw-685

Unsteady State Heat Flow Through
Thin Sheets

Prepared For
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REPORT ON STUDIES OF MEASUREMENT OF THERMAL DIFFUSIVITY

October 15, 1963

INTRODUCTION

The method is based on the following considerations. A beam of radiation is allowed to fall on one side of a thin plate where it is partially or completely absorbed. It is conducted through to the other side and the conducting wave is reflected back and forth. In order to make a dynamic method the incoming beam is interrupted at an adjustable frequency so that the signal which is recorded is an A.C. signal. The method involves measurement of the amplitude of thermal variation at the two faces after equilibrium has been set up.

Figure 1 shows the curve on which the method is based. Complete details of the calculation will be given in the final report. The frequency will be changed through such a range that $\sqrt{\frac{\omega}{2\alpha}} a$ varies from about $\frac{\pi}{10}$ to π . which means that the frequency is varied by a factor of 100 during any one run. The variation of the ratio of the temperature amplitude on the two faces of the sample over this frequency range should allow determination of the diffusivity.

TEMPERATURE MEASUREMENT

The first method tried to measure the surface temperature was to sputter a thermocouple on a microscope slide. One half of one face was sputtered with platinum and the other half with silver. These metals were chosen first not because of a large e.m.f., but because of ready availability and ease of sputtering. With such a thermocouple

on one face of a slide it was possible to measure, using a type K potentiometer and a D.C. amplifier, the temperature fluctuation when a radiant heat beam was interrupted up to 30 times per second.

REPORT ON STUDIES OF MEASUREMENT OF THERMAL DIFFUSIVITY

November 15, 1963

During this period the work was concentrated largely on methods of measurement of surface temperature. Thermocouples of several combinations of metals sputtered on to a glass slide were tried with varying degrees of success. However, it appeared that better results could be obtained by measuring the resistance of a platinum coating sputtered on the surface. The circuit used is shown in Fig. 2. The resistance R is chosen to have about the same resistance as the coating on the slide.

The first coating, sputtered on with a mask provided a back and forth pattern on the slide giving a total resistance of about 4000 ohms. This has the disadvantage that the surface of the sample is not opaque. Any visible or near infrared radiation goes through (not by conduction) to the back of the sample. The calculated curve is based on conduction alone.

A second slide was prepared with a platinum coating all over, thus preventing direct passage of radiation. This had a resistance of 80 ohms, which is in a quite usable range. At frequencies of about 30 cycles, readings have been obtained on both sides of a microscope slide.

Some difficulty encountered in pickup of stray 60 cycle signals was overcome by the use of a tuneable twin-T filter network between the amplifier and the oscilloscope. This allows pickup-free signal from the sample to be observed.

It is now planned to make determinations of diffusivity on various samples of increasing conductivity and decreasing thickness leading up to samples of beryllium oxide single crystals.

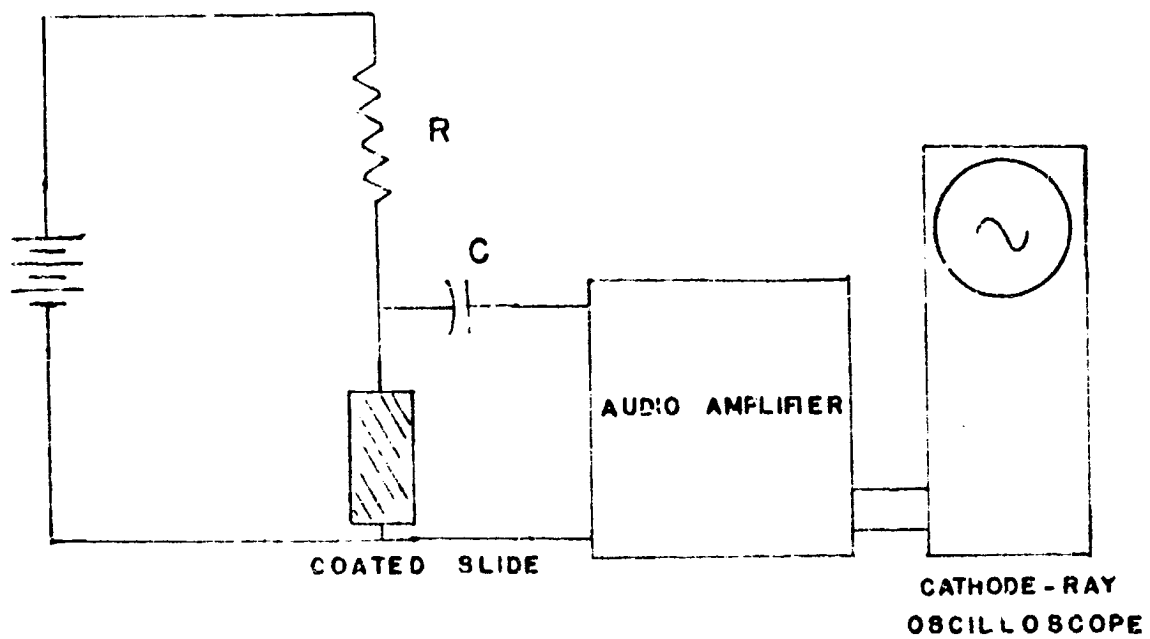


FIG. 2